Inorganica Chimica Acta, 11 (1974) L7 - L8

Pentafluorothiophenol Derivatives of Some Early Transition Metals

R. J. H. CLARK AND D. KAMINARIS

Sir Christopher Ingold Laboratories, Department of Chemistry, University College, London WC1H 0AJ, U.K.

(Received September 2, 1974)

Earlier work on the pentafluorothiophenoxide ion ($X^- = SC_6F_5^-$) has shown that it is closely similar to halide ions in the range of complexes it forms with metals in various oxidation states and in the structures and properties of these complexes.[1-8] No complexes of the ligand with the elements of groups IVA and VA have, however, previously been described. We report herein on the nature of the direct reactions of titanium, zirconium, hafnium, vanadium, and tin tetrachlorides and of niobium and tantalum pentachlorides with pentafluorothiophenol in an inert solvent. Complete (Ti, Hf, Sn or Nb) or partial (V or Ta) replacement of chloride by the pentafluorothiophenoxide ion is found to take place under these conditions.

The reactions studied are conveniently illustrated for the titanium case. By prolonged (*ca.* 7 day) heating of titanium tetrachloride under reflux in *n*-hexane with pentafluorothiophenol (mole ratio 1:4) slow elimination of hydrogen chloride takes place with the formation of a dark yellow solid. On the basis of its infrared spectrum this material is considered to be a mixture of the required fully substituted product and bis(pentafluorophenyl)disulphide (a common side product of the reactions of pentafluorothiophenol). The most satisfactory method for purification of the product was found to be vacuum sublimation at *ca.* 45 °C, under which conditions the bis(pentafluorophenyl)disulphide sublimed first, followed later by a pure sample of the required compound $Ti(Sc_6F_5)_4$; the latter is a pale yellow crystalline solid which is presumed to have a tetrahedral TiS_4 skeleton. The overall reaction scheme, which clearly takes place stepwise owing to the variety of colours of the reaction mixture during the reflux, is thus formulated as follows:

$$TiCl_4 + 4C_6F_5SH \rightarrow Ti(SC_6F_5)_4 + 4HCl$$

The infrared spectrum of the compound indicates the presence of the coordinated pentafluorophenoxide group, particularly from shifts in the frequencies of the strong bands in the regions of 1090, 985 and 859 cm^{-1}.

The mass spectrum of the compound did not show a peak corresponding to the parent ion, although this is not uncommon for sulphur-donor complexes.[9] The most prominent features of the mass spectrum were peaks with m/e values corresponding to the ions $(C_6F_5S)_2^+$, $(C_6F_5)_2S^+$, $(C_6F_5)_2^+$ and TiS_2^+.

The compound appears to be thermally stable up to 70 °C, but above this temperature decomposition takes place according to the reaction schemes

$$Ti(SC_6F_5)_4 \rightarrow TiS_2 + 2(C_6F_5)_2S$$

and

$$Ti(SC_6F_5)_4 \rightarrow TiS_2 + (C_6F_5S)_2 + (C_6F_5)_2$$

The ^{19}F nmr spectrum of the complex in chloroform (hexafluorobenzene as internal standard, $\delta = 162.9$) indicated chemical shifts of 149.0 and 160.6 (relative to $CCl_3F = 0$) characteristic of $[C_6F_5S]_2$; this indicates that the compound decomposes in solution.

The compound does not behave like a Lewis acid towards any common ligands such as triphenylphosphine, pyridine or dipyridyl. Thus either for steric or electronic reasons, the titanium atom in this complex is coordinatively saturated.

The other compounds[10] were prepared by essentially the same procedure. The compound $Sn(SC_6F_5)_4$ has been previously prepared and partially characterised by Peach;[5] his preparative route involved treatment of dilute HCl solutions of stannic chloride with pentafluorothiophenol over a period of 15 days. We find that the compound may be much more rapidly prepared by direct reaction of stannic chloride with pentafluorothiophenol in *n*-hexane (12 hr reflux, 80 °C). The compound was separated from some bis(pentafluorophenyl)disulphide by vacuum removal of the latter at *ca.* 25 °C. It is a yellow solid, mp *ca.* 145 °C.

Under comparable preparative conditions, the chloride in vanadium tetrachloride is only partly displaced by the $SC_6F_5^-$ ion leading to a dark brown product which could not be completely characterised. In the case of $HfCl_4$, $ZrCl_4$, ZrI_4, $NbCl_5$ and $TaCl_5$, the analogous reactions were carried out by use of dry chloroform or dry dichloromethane as solvent. The reaction mixtures were held under reflux for

8 - 10 days while at the same time a slow stream of dry nitrogen was passed through in order to assist the removal of the hydrogen chloride. In all cases, extensive colour changes took place and in some cases $(C_6F_5S)_2$ (and possibly other sulphur-containing species) were formed. The latter were generally removed by vacuum sublimation, and the required compound was filtered from any insoluble material and isolated by low temperature (solid CO_2) crystallisation. In this way, the compounds $Hf(SC_6F_5)_4$ (white, mp. 122 - 4 °C), $Nb(SC_6F_5)_5$ (white, mp. 98 - 100 °C) and $TaCl_3(SC_6F_5)_2$ (red-brown, mp. 136 - 7 °C) were obtained; no product could be isolated by use of either $ZrCl_4$ or ZrI_4 as starting material, and we could not succeed in the complete displacement of chloride from $TaCl_5$. The sensitivities of the compounds to air increase in the order $Sn < Ti < Hf \sim Nb < Ta$. The other properties of these compounds, including their mass spectral fragmentation patterns, their lack of Lewis acidity, and their apparent instability in solvents suitable for ^{19}F nmr studies were similar to those of the titanium compound.

It is concluded that the pentafluorothiophenoxide ion, which was already known to have pseudo-halide properties with non-metals and middle and late transition metals, also behaves like a pseudo-halide with the early transition elements.

Experimental

All reactions were carried out under dry nitrogen in vigorously dried solvents and by use of an apparatus and techniques described previously.[11]

Infrared spectra were recorded on a Perkin–Elmer 225 spectrometer, ^{19}F nmr spectra on a Varian HA 100 spectrometer, and mass spectra on an AEI MS12 spectrometer (ionizing potential 70 eV, source temperature 30 - 40 °C (Ti), and up to 140 °C for some of the other compounds).

One of us (D. K.) thanks the Royal Society for financial support. We are indebted to Dr. M. Coles and J. A. Stockwell for assistance with this work.

References

1 W. Beck and K. H. Stetter, *Inorg. Nucl. Chem. Letters, 2,* 383 (1966).
2 W. Beck, K. H. Stetter, S. Tadros and K. E. Schwarzhans, *Chem. Ber., 100,* 3944 (1967).
3 R. S. Nyholm, J. F. Skinner and M. H. B. Stiddard, *J. Chem. Soc.(A),* 38 (1968).
4 M. E. Peach, *Can. J. Chem., 46,* 211 (1968).
5 M. E. Peach, *Can. J. Chem., 46,* 2699 (1968).
6 J. Cooke, M. Green and F. G. A. Stone, *J. Chem. Soc.(A),* 170 (1968).
7 B. R. Hollebone and R. S. Nyholm, *J. Chem. Soc.(A),* 332 (1971).
8 M. Muller, R. J. H. Clark and R. S. Nyholm, *J. Chem. Soc. (Dalton),* to be published.
9 J. A. Douek and J. T. Spickett, *J. Inorg. Nucl. Chem., 35,* 511 (1973).
10 The compounds have been analysed for carbon, sulphur and metal atoms, *viz.* for $Ti(SC_6F_5)_4$. Found: C, 34.6; S, 16.3; Ti, 5.4. $C_{24}F_{20}S_4Ti$ requires C, 34.2; S, 15.2; Ti, 5.6%).
11 R. J. H. Clark and M. Coles, *J. Chem. Soc. (Dalton),* 2454 (1972).